CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS

Electronegativity Effects on B^{11} Chemical Shifts in Tetrahedral BX_4^- Ions

BY RALPH J. THOMPSON[1a] AND JEFF C. DAVIS, JR.[1b]

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The boron chemical shifts of a number of tetrahedral ions of the type BX_4^- were determined where X may be halide, alkyl, aryl, alkenyl, etc. In several cases, the shifts were limiting values which were observed to be dependent on the concentration of X^- ions in the solution. The latter were the tetrahaloborate anions with the exception of BF_4^-. The chemical shifts of these ions when measured in their respective liquid hydrogen halide solvents were almost the same as the limiting shifts observed in methylene chloride, but generally higher. The observed chemical shifts of all the tetrahedral BX_4^- anions were inferred to be an algebraic sum of inductive and paramagnetic components, even in the case of the alkyl derivatives. The inductive component is assumed to be a linear function of the valence state electronegativity of the atoms bonded directly to the boron and the paramagnetic contribution is assumed to be directly proportional to the π chemical shifts of the corresponding ternary borane.

Introduction

It might be anticipated that the shielding of the boron nucleus in tetrahedral BX_4^- ions is solely a function of the electronegativity of the group X, or essentially that of the atoms bonded directly to the boron. Since boron is a first row element and apparently has no low-lying empty d orbitals with which X could "back-coordinate," then this latter effect might be eliminated as a factor in the shielding.

Ternary boranes (represented here as BX_3) have a planar sp^2 configuration for boron with a vacant p orbital perpendicular to the plane of the molecule. Thus the boron chemical shifts of these compounds are affected greatly by delocalization of lone-pair electrons on atoms adjacent to the boron. Good and Ritter[2] have shown that in a number of trigonal boron compounds the observed boron chemical shift can be represented as an algebraic sum of an inductive contribution and a π-donor contribution, *i.e.*, by the equation

$$\delta = \delta_\sigma + \delta_\pi \tag{1}$$

where δ_σ is a linear function of the electronegativity belonging to the substituent atom or group and δ_π represents an increment of shielding arising from delocalization and is proportional to the π-electron density on the boron atom.

In this work a relationship is established between the boron chemical shifts of BX_4^- anions and the valence state electronegativity of the atoms bonded directly to the boron.

The electronegativity valves calculated by Huggins[3] from thermochemical data are used here and are in very close agreement with those of Dailey and Shoolery[4] which were obtained by n.m.r. techniques. The latter approach also provided electronegativity values for sp^2 carbon. The cases of high shielding in ions such as BF_4^- and $B(C{\equiv}CC_6H_5)_4^-$ lend direct support to the argument that low-lying antibonding orbitals of the boron atom and anisotropies may contribute in some degree to a paramagnetic shift.

Experimental

Reagents and Spectra.—All n.m.r. boron chemical shifts were measured on a Varian DP-60 spectrometer at 19.3 Mc./sec. Values are reported in parts per million (p.p.m.) with boron trifluoride etherate as the external standard. Infrared spectra were obtained on a Beckman IR-7 spectrophotometer.

Elemental analyses were performed on compounds which could be isolated in the pure state. All reagents and products were handled in an inert atmosphere whenever required.

Low-Temperature Measurements.—The boron chemical shifts of the tetrahaloborates were observed in their respective liquid hydrogen halide in addition to other solvents. Low temperatures were obtained by passing nitrogen gas from a compressed tank through a copper coil immersed in a large dewar of liquid nitrogen. After passing through the coil the cold nitrogen gas was introduced into the sample probe between the poles of the electromagnet. The sample tube was in place in a glass dewar insert fabricated for this purpose. The temperature was monitored with a thermocouple and could be held constant to within less than 1°.

Tetrachloroborates.—Finely ground anhydrous tetramethylammonium chloride was placed in a glass Pyrex trap which was then immersed in a Dry Ice–acetone bath. Boron trichloride from a tank was allowed to condense in the trap until an excess was present. After standing for 15 min., the excess BCl_3 was allowed to evaporate at room temperature, leaving a white solid in the bottom of the trap. *Anal.* Calcd. for $N(CH_3)_4BCl_4$: C, 21.17; H, 5.34; N, 6.18. Found: C, 20.25; H, 5.31; N, 6.05.

Tetramethylammonium tetrachloroborate is hydrolyzed by water and reacts vigorously with alcohols. It is insoluble in hydrocarbons, chlorinated hydrocarbons, benzene, and ether. However, it dissolves readily in dimethyl sulfoxide. The B^{11} chemical shift of fresh solution was measured to be −6.84 p.p.m. After several hours the solution became gelatinous and several peaks were observed. Excess Cl^- could not be added because of the insolubility of available salts in this solvent.

The boron chemical shift of $N(CH_3)_4BCl_4$ (*ca.* 50 mg./ml.) was measured in liquid HCl at −100° and was determined to be −6.58 p.p.m. The addition of an excess of $(CH_3)_4NCl$ had no effect on the shift, whereas the continual addition of small amounts of chlorotriphenylmethane (trityl chloride, Eastman Organic Chemicals, Inc.) to a solution of BCl_3 in dry methylene chloride (δ −41.9 p.p.m.) gradually increased the chemical shift up to a limiting value of −6.74. The increasing shift had not leveled off before the solution had become saturated with the salt, however.

The infrared spectrum of $N(CH_3)_4BCl_4$ was characterized by an

(1) (a) From a dissertation accepted by The University of Texas in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) Department of Chemistry, University of South Florida, Tampa, Fla.

(2) C. D. Good and D. M. Ritter, *J. Am. Chem. Soc.*, **84**, 1162 (1962).

(3) M. L. Huggins, *ibid.*, **75**, 4123 (1953).

(4) B. P. Dailey and J. N. Shoolery, *ibid.*, **77**, 3977 (1955).

intense absorption at 698 cm.$^{-1}$ and one of lesser intensity at 670 cm.$^{-1}$, in good agreement with the results of Kemmitt, *et al.*,[5] who reported values of 703 and 668 cm.$^{-1}$ for $KBCl_4$.

Tetrabromoborates.—Ten grams of pyridinium bromide was added to a round-bottomed flask, dissolved in dry methylene chloride, and transferred to a drybox. Six ml. of BBr_3 (K and K Laboratories, Inc.) was added and a white precipitate formed rapidly. The precipitate was washed three or four times with CH_2Cl_2 to remove any excess BBr_3 or pyridinium bromide. *Anal.* Calcd. for $C_5H_5NHBBr_4$: C, 14.62; H, 1.47; N, 3.41. Found: C, 14.53; H, 1.59; N, 3.30.

The infrared spectrum of pyridinium tetrabromoborate (Nujol mull) showed a strong absorption at 587 cm.$^{-1}$, which agrees favorably with the value of 593 cm.$^{-1}$ given for BBr_4^- by Waddington.[6] A solution prepared from equimolar quantities of $(C_2H_5)_4NBr$ and BBr_3 in methylene chloride showed a strong absorption peak at 590 cm.$^{-1}$.

The B^{11} chemical shift for pyridinium tetrabromoborate in dimethyl sulfoxide was +2.07 p.p.m. Addition of excess pyridinium bromide increased this to approximately +13 p.p.m. but further shift of the resonance was prevented by the insolubility of the bromide. The boron chemical shift of approximately 0.1 g. of pyridinium tetrabromoborate in 1 ml. of liquid HBr at −75° was +23.6 p.p.m. Another 0.1 g. of the same solute was dissolved in 1 ml. of purified nitrobenzene. The n.m.r. spectrum showed a single sharp peak which moved to higher field as more pyridinium bromide was added to the solution until a limiting value of +24.1 p.p.m. was reached, thus demonstrating a marked dependence on bromide ion concentration. This bromide ion dependence was lacking in liquid HBr. The boron chemical shift of BBr_3 in methylene chloride was −39.5 p.p.m. When anhydrous tetraethylammonium bromide was added to this solution to the point of saturation, a shift of +23.8 p.p.m. was observed. The trityl and tropenium salts were prepared as described by Harmon and Harmon.[7] The shifts measured in liquid HBr were +23.9 and +24.2 p.p.m., respectively.

Tetraiodoborates.—Waddington,[6] in a short communication, reports the preparation of tetramethyammonium, tetraethylammonium, and pyridinium tetraiodoborates from the appropriate iodide and boron triiodide in liquid hydrogen iodide as a solvent. No details of preparation or characterization were given. Harmon and Cummings[8] have reported the preparation of the tropenium and triphenylcarbonium tetraborates and the B^{11} chemical shift as +112.2 p.p.m.

The boron chemical shift of tetraiodoborate ion was measured using a mixture of boron triiodide and tetrabutylammonium iodide in methylene chloride. The shift varied from about +66 p.p.m. (for approximately equal weights of the two reactants) up to a final value of +127.5 p.p.m. as more of the quaternary ammonium iodide was dissolved in the solution. This limit was reached before saturation.

Anhydrous hydrogen iodide (Matheson Co., Inc.) was condensed into an n.m.r. tube containing about 0.1 g. of BI_3 (K and K Laboratories, Inc.) and a large excess of tetrapropylammonium iodide while the sample tube was immersed in a chlorobenzene slush bath. After the condensation of about 1 ml. of HI from the tank, the tube was capped and twirled rapidly back and forth to hasten solution of the solids. The boron chemical shift (measured at −43°) was +128 p.p.m. A second sample containing a larger amount of the quaternary ammonium iodide showed no detectable change in the shift.

The infrared spectrum of the BI_3–tetrapropylammonium iodide solution in methylene chloride showed a relatively strong absorption at 515 cm.$^{-1}$, which compares with the reported value of 517 cm.$^{-1}$.[9] Attempts to isolate pure tetraiodoborates from solution (other than the tropylium salt) were unsuccessful and resulted in a copius loss of iodine.

Tetrafluoroborate.—A sample of triphenylmethyl fluoroborate,[10] $(C_6H_5)_3C^+BF_4^-$, was obtained in a pure form and is quite soluble in methylene chloride. The boron chemical shift in this solvent was +1.55 p.p.m. The addition of a small amount of $(C_4H_9)_4N^+F^-$ did not affect this value.

Pure KBF_4 was obtained by the neutralization of HBF_4, which was produced by the reaction of aqueous hydrofluoric acid and granular boric acid.[11] The boron chemical shift of KBF_4 in liquid HF at −5° was +1.81 p.p.m. An n.m.r. sample tube made of Teflon was used for hydrogen fluoride work. A duplicate sample containing lithium fluoride showed no detectable change in the chemical shift. A solution of BF_3 bubbled into liquid HF at −80° gave a shift of +1.76 p.p.m.

Tetramethylborate.—Lithium tetramethylborate, $Li^+B(CH_3)_4^-$, was prepared by the method described by Hurd.[12] A weighed sample of the white solid was allowed to react with an excess of standard sulfuric acid and the excess titrated with standard base. Acidification of the solid liberated methane and trimethylborane. A molecular weight of 77.81 was determined; the actual formula weight is 77.90.

The boron chemical shift of an ether solution of $Li^+B(CH_3)_4^-$ was +20.2 p.p.m. A chemical shift of −86.2 p.p.m. was observed for a sample of the original ether distillate containing the trimethylborane.

Tetraethylborate.—Triethylborane, b.p. 95°, was prepared by the action of BF_3 etherate on ethylmagnesium bromide in ethyl ether. After distillation of the product (B^{11} shift −86.6 p.p.m.) ethyllithium was added dropwise. The B^{11} chemical shift of this solution was +17.48 p.p.m. Attempts to isolate pure $LiB(C_2H_5)_4$ were unsuccessful but comparison of the shifts with the methyl analog indicates the tetrahedral ion was formed. The resonance peak was also much sharper than that of the corresponding triethylborane, indicating a lessening of quadrupolar interaction because of tetrahdral symmetry.

Tetravinylborate.—Lithium tetravinylborate was prepared according to the procedure of Seyferth,[13,14] which employs the reaction of vinyllithium with trivinylborane. The triphenylmethylarsonium tetravinylborate derivative was also prepared as described.[14] After drying under vacuum over P_2O_5 a melting point of 141.3° was observed, which was in close agreement with the reported value of 142.5–144°.

A boron chemical shift of an ether solution of $Li^+B(CH{=}CH_2)_4^-$ was observed to be +16.1 p.p.m. The resonance was sharp.

Tetraallylborate.—Pure $LiB(CH_2CH{=}CH_2)_4$ was not isolated but a solution was prepared from triallylborane (B^{11} shift −87.4 p.p.m.) and allyllithium which showed a B^{11} chemical shift of +16.8 p.p.m. and characteristic olefinic C—H stretching frequencies as well as C=C stretching motions. The resonance peak was sharp.

Other Tetraalkylborates.—Both *n*-propyl and *n*-butyl trialkylboranes were prepared from the reaction of BF_3 etherate and the appropriate alkylmagnesium bromide. The B^{11} shifts of their ether solutions were −86.6 and −86.5 p.p.m., respectively, and were broad as is characteristic of trigonal boron compounds. Excess alkyllithium resulted in peaks at +17.5 and + 17.6 p.p.m. Solutions containing an excess of the trialkylborons showed both the broad low-field peak and the sharp high-field peak simultaneously, indicating no exchange between the species or at least a very slow exchange.

Discussion

Solvent Effects.—Information prior to this investigation indicated clearly that the boron chemical shifts of

(5) R. D. Kemmitt, R. S. Milner, and E. W. Sharp, *J. Chem. Soc.*, 111 (1963).

(6) T. C. Waddington and J. A. White, *Proc. Chem. Soc.*, 315 (1960).

(7) K. M. Harmon and A. B. Harmon, *J. Am. Chem. Soc.*, **83**, 865 (1961).

(8) K. M. Harmon and F. E. Cummings, *ibid.*, **84**, 1751 (1962).

(9) T. C. Waddington and F. Klanberg, *J. Chem. Soc.*, 2329, 2332 (1960).

(10) A generous sample was supplied by Dr. John Mahler of these laboratories.

(11) P. A. van der Meulen and H. L. Van Mater, *Inorg. Syn.*, **1**, 24 (1939).

(12) D. T. Hurd, *J. Org. Chem.*, **13**, 711 (1948).

(13) D. Seyferth and M. A. Weiner, *Chem. Ind.* (London), 402 (1959).

(14) D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

the tetrahaloborate ions are dependent on the concentration of halide ion in the solution,[15] with BF_4^- an apparent exception, and the particular solvent referred to was nitrobenzene. This lends strong evidence for the presence of the equilibrium

$$BX_4^- + \text{solvent} = BX_3\cdot\text{solvent} + X^-$$

Since only one peak is observed the rate of halogen exchange must be considerably larger than the magnitude of the difference in the resonance frequencies of the two species containing boron. This investigation has shown unambiguously that this phenomenon is also present when the solvent methylene chloride is used. Thus a "limiting shift" can be approached for the BX_4^- ion by increasing the concentration of halide ion up to the limits of solubility.

It is interesting to note that the limiting shifts of the tetrahaloborate ions in organic solvents were in close agreement with those measured in their respective hydrogen halide solvents where further addition of halide ion had no effect. The latter are generally slightly higher than shifts measured in other solvents and might be considered "pure" limiting shifts for the ionic species.

Electronegativity Effects.—Examination of the measured B^{11} chemical shifts reveals that there is no direct correlation between the B^{11} shifts and the electronegativities of the substituents although the halide ions BI_4^-, BBr_4^-, and BCl_4^- are in the expected order. The BF_4^- ion, for example, has an unexpectedly high shift as does the $B(C{\equiv}CC_6H_6)_4^-$ ion.

The work of Good and Ritter[2] suggests the magnitude of inductive and delocalization contributions to the observed boron chemical shifts of a series of trigonal boron compounds, here designated by BX_3. The observed chemical shift was represented by eq. 1, where δ_σ is a linear function of the valence state electronegativity of the atoms bonded directly to the boron and δ_π is proportional to the magnitude of electron delocalization. Although such an interpretation of the diamagnetic and paramagnetic contributions to shielding is undoubtedly oversimplified, it was found by Good and Ritter to correspond approximately to other estimates of π bonding in ternary boron compounds.

The chemical shifts of boron in the tetrahedral ions is certainly more complicated in view of the absence of π bonding in the traditional sense utilizing bonding orbitals. However, it is of interest to extend this approach to the tetrahedral BX_4^- ions. The observed chemical shifts can be represented by

$$\delta = A - BE_x + \delta_{para} \qquad (2)$$

where the term $(A - BE_x)$ corresponds to δ_σ for the BX_4^- ion and depends on the electronegativity, E_x, of the atoms bonded directly to the boron. If it is assumed that δ_{para}, the paramagnetic contribution, is directly proportional to the trigonal boron π-bond shifts of Good and Ritter

$$\delta_{para} = C\delta_\pi$$

then eq. 2 can be written as

$$\delta = A - BE_x + C\delta_\pi \qquad (3)$$

The values of the constants A, B, and C were determined by substituting the observed shifts of the tetrahaloborate ions BF_4^-, BCl_4^-, and BBr_4^- along with the corresponding halogen electronegativities and

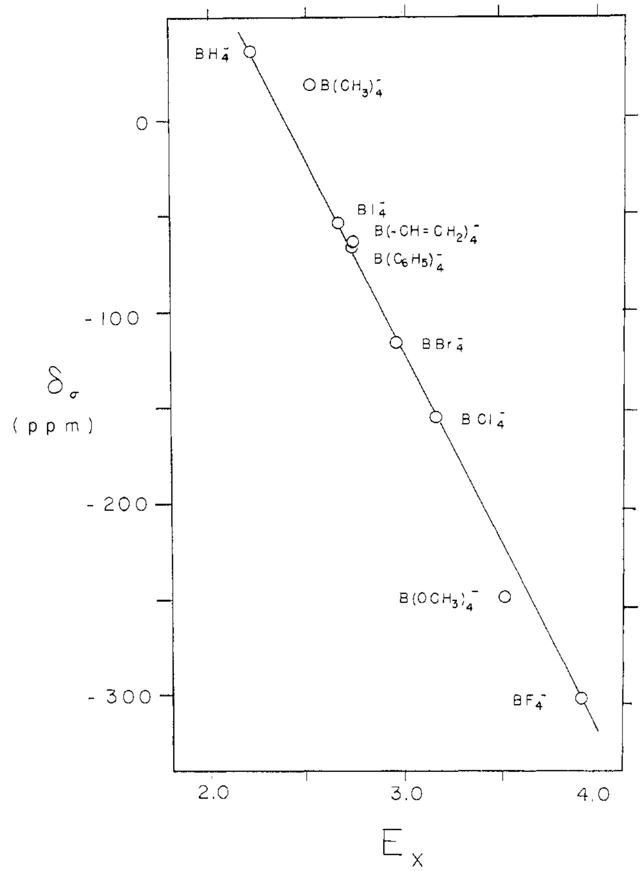

Figure 1.—Dependence of calculated σ contribution to B^{11} chemical shift on electronegativity of substituents in BX_4^- ions.

Table I

Chemical Shift Data for BX_4^- Ions

BX_4^-, X =	Electroneg.	δ_{calcd}	δ_{obsd}	δ_σ	δ_{para}	δ_π (BX_3)[a]
F	3.90	...[b]	1.8	−308	310	174
Cl	3.15	...[b]	−6.6	−156	150	85
Br	2.95	...[b]	23.9	−114	138	77
I	2.65	127	128.0	−54	181	101
H	2.20	37	38.2	37	1[f]	0
C_6H_5	2.70	6	6.8	−64	70	39
C_2H_3	2.70	15	16.1	−64	79	44
CH_3	2.50	−24	20.5	−24	44[f]	0
OCH_3[c]	3.50	20	−2.9	−249[g]	246	137
$C{\equiv}CC_6H_5$[d]	3.29	...[e]	13.2	−183	214	...[e]

[a] Values determined by Good and Ritter.[2] [b] The observed shifts were used to calculate A, B, and C of eq. 4. [c] Shift measured by Onak, *et al.*[16] [d] Shift measured by Phillips, *et al.*[17] [e] Chemical shift not available for BX_3. [f] Determined by difference. [g] Calculated using corrected electronegativity of oxygen (3.62) for increase in B–O–CH_3 angle from steric hindrance.

(15) H. Landesman and R. E. Williams, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

(16) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

(17) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

the π chemical shifts of the boron trihalides.[2] This gives the equation for the observed shift (in p.p.m.)

$$\delta = 480 - 201.5E_x + 1.79\delta_\pi \qquad (4)$$

The agreement between this equation and all of the BX_4^- chemical shifts which were measured can be seen in Figure 1, where $\delta_\sigma = \delta_{obsd} - 1.79\delta_\pi$. All of the alkyls have similar shifts to $B(CH_3)_4^-$ in this figure. The values of all of the parameters of interest are collected in Table I.

Some mention should be made of the observed chemical shift of the ion $B(C{\equiv}CC_6H_6)_4^-$ which has been reported.[18] A value of +31.2 p.p.m. shows an unusually high shielding of the boron nucleus considering that four sp carbons are attached to the boron. The electronegativity of an sp carbon atom has been calculated and a value of 3.29 reported,[19] which is even more electronegative than chlorine.

It is very likely that substituent electronegativity contributes to both the diamagnetic and paramagnetic shielding effects in the BX_4^- ions. It is of interest that those ions which deviate the most from a direct correlation with substituent electronegativity are also those which have large π-bond contributions in the trigonal compounds. Several investigators[19–21] engaged in n.m.r. studies of saturated haloalkanes have invoked double-bond and no-bond structures. It would be more correct, perhaps, to describe the situation as a contribution to the total molecular wave function by low-lying antibonding orbitals which are usually ignored in a simple structural picture.[22,23] It is also likely, however, that a variety of effects caused by bond anisotropies and low-lying excited electronic states are important factors. It is not surprising that these are most prominent in the substituents which have π-orbital systems. A thorough understanding of the shifts in terms of actual calculations would be difficult.

A similar study of the Al^{27} chemical shifts in the analogous AlX_4^- ions is now being undertaken to determine the effects of the empty Al d orbitals.

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(18) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).
(19) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).
(20) R. Livingston, *ibid.*, **57**, 496 (1953).
(21) R. S. Smith and E. A. Smith, *ibid.*, **63**, 1701 (1959).
(22) J. F. A. Williams, *Trans. Faraday Soc.*, **57**, 2089 (1961).
(23) G. Kohnstam, *J. Chem. Soc.*, 2066 (1960).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES, CALIFORNIA 90007

Lewis Acid–Base Reactions among Dimethylaminoboron Hydrides[1]

BY ANTON B. BURG AND JAGTAR S. SANDHU

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The dimethylaminoboron hydrides related to diborane form a system of Lewis acids and bases, the interconversion of which can be described as addition or removal of BH_3 groups. The first-stage action of $[(CH_3)_2N]_3B$ to remove BH_3 from $(CH_3)_3N\cdot BH_3$ is not appreciably reversible, but the second stage, in which $[(CH_3)_2N]_2BH$ and $(CH_3)_3N\cdot BH_3$ form $2(CH_3)_2NBH_2$ and $(CH_3)_3N$, is reversible with $\Delta F° = 13.95 - 0.0330T$ kcal. Our base$\cdot(CH_3)_2NB_2H_5$ adducts show vapor-phase dissociation increasing in the order pyridine, $(CH_3)_3P$, 2-methylpyridine, $(CH_3)_3N$; and $(CH_3)_2PH\cdot(CH_3)_2NB_2H_5$ fails to exist in the vapor phase but forms a partially dissociated liquid. All five of these adducts on heating react further to form $(CH_3)_2NBH_2$ and base$\cdot BH_3$, without reversal. The adducts $CH_3PH_2\cdot(CH_3)_2NB_2H_5$ and $(CH_3)_2PCF_3\cdot(CH_3)_2NB_2H_5$ are still more easily dissociated, and their conversion to BH_3 complexes and $(CH_3)_2NBH_2$ is reversible with $\Delta F° = 10.61 - 0.0268T$ and $6.59 - 0.01943T$ kcal., respectively. It is quite apparent that diborane is a much stronger Lewis acid than $(CH_3)_2NB_2H_5$.

Earlier studies of aminoboron hydrides[2,3] indicated the following pattern of acid–base reactions wherein amino groups exert a basic function while boron (here represented as a BH_3 group transferring hydride) accounts for Lewis acid action (eq. 1). In this pattern, of course, the BH_3 group is added in the direction of the nearest arrow.

$$\begin{array}{ccccc} 6(CH_3)_2NB_2H_5 & \overset{6BH_3}{\rightleftarrows} & 6(CH_3)_2NBH_2 & \overset{3BH_3}{\rightleftarrows} & 3[(CH_3)_2N]_2BH \\ & & \downarrow\uparrow & & \downarrow\uparrow{\scriptstyle BH_3} \\ & & 3[(CH_3)_2NBH_2]_2 & & 2[(CH_3)_2N]_3B \end{array}$$

Implicit in this system is the neutralization reaction

$$[(CH_3)_2N]_3B + (CH_3)_2NBH_2 \longrightarrow 2[(CH_3)_2N]_2BH \qquad (1)$$

which we now have found to be essentially irreversible. For a fuller study of the system, we have also used $(CH_3)_3N\cdot BH_3$ as a source of BH_3; and a series of bases having different strengths served to remove BH_3 from $(CH_3)_2NB_2H_5$; also, equilibrium constants were determined wherever feasible. Thus reaction 2, pre-

(1) We gratefully acknowledge the support of this research through Office of Naval Research Contract No. Nonr-228(13). Reproduction is authorized for any purpose of the United States Government. We are grateful also to the National Science Foundation for aiding the purchase of a Beckman IR7 spectrophotometer, through Grants G-14665 and GP-199.

(2) A. B. Burg and C. L. Randolph, Jr., *J. Am. Chem. Soc.*, **71**, 3451 (1949).
(3) A. B. Burg and C. L. Randolph, Jr., *ibid.*, **73**, 953 (1951).